

## Facile manufacture of high-purity $\text{CuSO}_4$ from waste Cu-containing paint residue using combined processes of $\text{H}_2\text{SO}_4$ leaching and extraction stripping

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### ABSTRACT

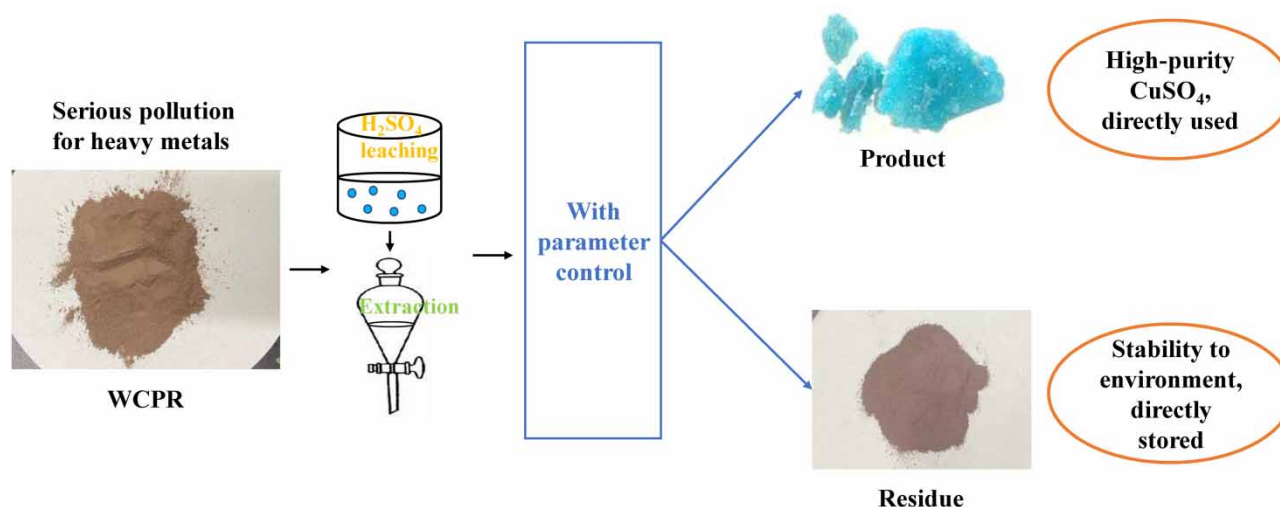
Waste copper-containing paint residue (WCPR) represents a typical hazardous waste containing both toxic organic substances and toxic heavy metals, but there are few reports on the recycling of heavy metals. The recovery of Cu from WCPR by  $\text{H}_2\text{SO}_4$  leaching–extraction–stripping has the advantages of eco-friendliness, simplicity of operation, and high value-added product. The results show that under the optimal conditions, the leaching rate of Cu in WCPR is 94.31% (18.02 g/L), while the extraction and stripping rates of Cu in the leaching solution are 99.46 and 95.32%, respectively. Due to the high concentration of  $\text{Cu}^{2+}$  with fewer impurities in the stripping solution, the stripping solution is heated, evaporated, cooled, and crystallized to successfully produce high-purity dark blue  $\text{CuSO}_4$  crystal, accomplishing the high-value recycling of Cu in WCPR. In addition, the leach residue of WCPR contains acrylic resin and  $\text{SiO}_2$ , which can be used in cement kilns for incineration, thus realizing the overall recycling and utilization of WCPR.

**Key words:** Cu recycling,  $\text{H}_2\text{SO}_4$  leaching, hazardous waste, mechanism, regeneration of  $\text{CuSO}_4$ , waste copper-containing paint residue

### HIGHLIGHTS

- The process of Cu recovery from waste copper-containing paint residue was first proposed to regenerate  $\text{CuSO}_4$ .
- Using leaching–extraction–stripping to recover Cu has the advantages of eco-friendliness and high value-added product.
- The stripping solution without impurities can be used directly to regenerate  $\text{CuSO}_4$ .
- The resulting residue with no environmental risk can be cement kiln incineration.
- The process can eliminate Cu pollution and recover Cu resource.

### GRAPHICAL ABSTRACT



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## 1. INTRODUCTION

With the growth of China's maritime commerce and shipbuilding industry, ship coating has become a crucial and significant step in ship construction. It is also critical for safeguarding against corrosion in severe sea conditions and prolonging the vessel's lifespan (Maia *et al.* 2015; Wang & Dai 2020). At present, due to the existence of new antifouling agents such as poor antifouling effect, short antifouling time, and relatively single target marine pollution organisms, the commercial antifouling paint used for ship coating is still mainly copper ( $\text{Cu}_2\text{O}$ ) oil-soluble paints, and its unique  $\text{Cu}_2\text{O}$  components can form copper complexes after contact with seawater, which react with oxygen in seawater to form divalent copper ions, thereby forming a thin toxic micro-layer on the coating surface. The Cu ions in the microlayer can enter biological cells and poison dead organisms, thereby achieving antifouling effects (Blanca 2008; Qian *et al.* 2015; Mohamed *et al.* 2015; Chen *et al.* 2021). Therefore, Cu-containing antifouling paints will still be the most mainstream antifouling coatings on the market for a long time to come.

During the coating process of ships, the Cu-containing antifouling paint will not be fully attached to the hull, but a large amount of paint mist is generated due to splashing. Therefore, the coating rate is relatively low, even with advanced electrostatic spraying. Only about 60% of the coating process is effective, and most of the paints used in the spraying process are splashed in the spraying room (Dvořák & Jandová 2005; Fu 2012). Currently, most of the coating processes in China absorb the paint mist using the circulating water in the spraying room, causing it to coalesce into paint residue (Salihoglu & Salihoglu 2016). In order to keep good antifouling performance of the ship, it is necessary to repaint it regularly, thus making a large amount of waste Cu-containing paint residue (WCPR). At present, China alone produces about 100,000 tons of WCPR annually, which contains not only a large amount of organic matter but also a variety of heavy metals such as Zn, Fe, and copper (5–10%). This amount is much higher than the average grade of ores in China. According to the 'National Hazardous Waste List of the Ministry of Environmental Protection,' this residue belongs to HW21 dyes and paints hazardous waste (Fu 2012). If WCPR is not effectively treated, it will cause severe damage to both the ecological environment and human health. Therefore, it is of great significance to explore a reasonable disposal method for WCPR to solve the environmental pollution problem from the source.

As WCPR contains a large number of organic compounds and heavy metal ions, these components usually have irreversible toxic effects on the environment and the human body (Xing *et al.* 2018). In addition, due to the long-term coexistence of a large number of toxic substances in WCPR, there is a possibility of synergistic effects, so that it has a higher degree of toxicity, irritation, and hazard (Wang & Dai 2020). There is still a long way to go to achieve the reasonable disposal of WCPR. At present, the main disposal methods of WCPR are still landfilling (Song *et al.* 2005; Arce *et al.* 2010) and incineration (Saft 2007; Rosli *et al.* 2018). However, both not only fail to achieve the utilization of valuable components in WCPR, resulting in the loss of its resource value, but also cause serious environmental pollution. For example, the incineration method has a high cost and is prone to secondary environmental problems, and the landfill method not only requires a large amount of land but also has safety hazards like leachate leakage. Therefore, to maximize the resource utilization of WCPR, some scholars have started to study the recovery of valuable components, but their focus is still on the recycling and utilization of resin and organic matter (Gerace & Gerace 1992; Avci *et al.* 2017). However, there are few reports on the recovery of heavy metals from WCPR.

Aiming at the aforementioned problems, this article proposes a process of  $\text{H}_2\text{SO}_4$  leaching–extraction–stripping to prepare  $\text{CuSO}_4$ , so that Cu of WCPR undergoes the processes of dissolution, extraction, and stripping in the reaction, and finally outputs in the form of regenerated  $\text{CuSO}_4$ . The  $\text{H}_2\text{SO}_4$  leaching residue does not contain heavy metals and can be used in cement kiln incineration (Yuan & Wang 2015; Zhao *et al.* 2017; Wang *et al.* 2018), so as to realize the recovery and utilization of WCPR. Therefore, this method can maximize the economic value of the recycled products under the premise of environmental safety, simple operation, rapid leaching, and extremely short process flow, thus realizing the purpose of reduction, harmlessness, and resource utilization of WCPR. To further realize a precise and quantitative regulation of the whole process, five aspects have been carried out. (1) the optimal process conditions for leaching Cu from WCPR with  $\text{H}_2\text{SO}_4$ ; (2) the optimal extraction and stripping conditions for Cu; (3) the change of shape, size, phase, and elemental composition of WCPR before and after  $\text{H}_2\text{SO}_4$  leaching; (4) the utilization of the  $\text{H}_2\text{SO}_4$  leaching residue of WCPR; (5) the  $\text{H}_2\text{SO}_4$  leaching solution is applied to fabricate an important chemical product  $\text{CuSO}_4$  by using precipitation to achieve the high-value utilization of Cu in WCPR.

## 2. EXPERIMENT

### 2.1. Experimental materials and reagents

WCPR was obtained from a hazardous waste treatment company in Shandong Province. It was dried in an oven at 80 °C to constant weight and then ground through a 60-mesh sieve to obtain a powder with a particle size of 0.25 mm, which was

finally stored in a sealed reagent bottle for subsequent experiments. The reagents used in the experiments were HCl, HNO<sub>3</sub>, HF, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, extractant (LIX984), and sulfonated kerosene (DT100), all of which were analytically pure, and all solutions were prepared with deionized water.

## 2.2. Experimental methods

### 2.2.1. H<sub>2</sub>SO<sub>4</sub> leaching of Cu in WCPR

The H<sub>2</sub>SO<sub>4</sub> leaching experiment was carried out in a conical flask. A certain amount of dried WCPR was placed in the H<sub>2</sub>SO<sub>4</sub> solution that had been raised to a specified temperature and leached on a constant temperature water bath shaker for a certain period of time to investigate the effects of H<sub>2</sub>SO<sub>4</sub> concentration, solid-liquid ratio (S/L), leaching temperature, stirring speed, and leaching time on the leaching rate of Cu. At the end of the leaching, the leaching solution and the residue were separated for the corresponding characterization.

### 2.2.2. Extraction of copper from the leaching solution

The extraction experiment was carried out in a conical flask. A certain amount of leaching solution adjusted to the desired pH (adjusted by 1 mol/L Na<sub>2</sub>SO<sub>4</sub> solution) was placed in the LIX984 diluted with DT100 that had been raised to a specified temperature and extracted on a constant temperature water bath shaker (50 r/min) for a certain period of time to investigate the effects of pH, the volumetric ratio of the organic phase to the aqueous phase (O/L), LIX984 concentration, and extraction time on the extraction rate of Cu. At the end of the reaction, a partition funnel was used to separate the two phases, the aqueous phase was used for iron removal and zinc precipitation (Davey & Scott 1976; Su *et al.* 2020), and the oil phase was used for the next step of the stripping experiment.

### 2.2.3. Regeneration of CuSO<sub>4</sub>

The stripping experiment (regeneration of CuSO<sub>4</sub>) was carried out in a conical flask. A certain amount of extracted oil phase was placed in the H<sub>2</sub>SO<sub>4</sub> solution that had been raised to a specified temperature and reacted on a constant temperature water bath shaker (50 r/min) for a certain period of time to investigate the effects of H<sub>2</sub>SO<sub>4</sub> concentration, stripping time, and O/L on the copper stripping rate of Cu. At the end of the reaction, a partition funnel was used to separate the two phases: the aqueous phase was heated, evaporated, cooled, and crystallized to prepare CuSO<sub>4</sub> crystals, and the oil phase was reused for the extraction of Cu (Yi *et al.* 2019).

### 2.2.4. Leaching toxicity test of leaching residue

The leaching toxicity test was an important identification index of the toxicity properties of hazardous waste. The leaching toxicity for the leaching residue of WCPR was determined by using the method of Chinese standards (GB5085.3-2019 and GB16889-2008) as follows: deionized water was mixed with mixed acid (the mass ratio of H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> was 2:1) to a pH of 3.20 ± 0.05, and the solid waste was added at S/L of 1:10 (kg/L). It was placed on an overturning oscillation device with an oscillation speed of 30 ± 2 r/min and a temperature of 23 ± 2 °C and leached for 18 ± 2 h. The metal concentrations in the supernatant were determined and compared with the national standard limits (Tian *et al.* 2022).

All leaching experiments were conducted in triplicate, and the results were expressed as the arithmetic mean of three parallel experiments. The leaching/ extraction/stripping rate of Cu was calculated using the following formula:

$$\delta = \frac{C_i \times V}{mw} \times 100 \% \quad (1)$$

where  $\delta$  is the leaching/extraction/stripping rate of Cu,  $C_i$  is the concentration of different metal ions in the leaching solution (mg/L),  $V$  is the volume of the leaching solution (L),  $m$  is the mass of sample added (g), and  $w$  is the mass percentage of elements in the sample (wt.%).

## 2.3. Experimental characterization

The content or concentration of various metal ions was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8000, PerkinElmer, USA). The phase and structure of raw materials, various intermediates, and products were analyzed by X-ray diffraction (XRD; D8 Advance, Burker, Germany). The pH during leaching or reaction processes was detected and regulated by a pH meter (Mettler Toledo, S210, USA). The surface morphology and elemental distribution of the raw, intermediates, and products were investigated by scanning electron microscope (SEM) and mapping

analysis (SU8020, Hitachi Ltd, Japan). The organic compounds of the raw, intermediates, and products were detected by Fourier transform infrared spectrometer (FT-IR; Nicolet iS50, Thermo Fisher, USA).

### 3. RESULTS AND DISCUSSION

#### 3.1. Composition analysis of WCPR

The main element content in WCPR was determined by ICP-OES (after digestion by using HNO<sub>3</sub>-HCl-HClO<sub>4</sub>-HF (1:2:1:1 by volume) mixed solution) (Niu *et al.* 2021), and the phase composition was analyzed by XRD. Table 1 shows that the content of Cu/Zn/Fe in this material was high (9.55, 1.64, and 11.35%, respectively), which had a high recovery value. Figure 1 shows that Cu was mainly present in the form of Cu<sub>2</sub>O and Zn was mainly present in the form of ZnO in the WCPR. In addition to metal elements, a certain amount of SiO<sub>2</sub> was also present.

#### 3.2. H<sub>2</sub>SO<sub>4</sub> cycle-leaching for recovery of Cu

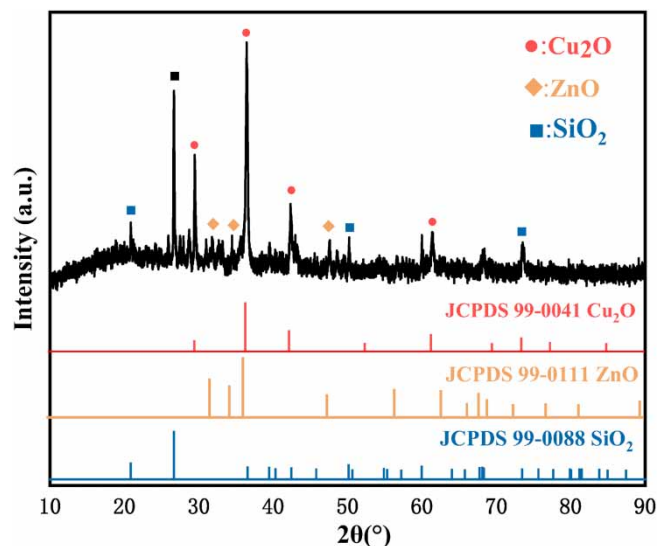
The significant factors such as H<sub>2</sub>SO<sub>4</sub> concentration, S/L, leaching time, leaching temperature, and stirring speed were selected to focus on their effects on the leaching rate of Cu, and the results are shown in Figure 2(a)–2(e), respectively.

Figure 2(a) shows the effect of different H<sub>2</sub>SO<sub>4</sub> concentrations (5–25%, v/v: 98 wt.% H<sub>2</sub>SO<sub>4</sub>, deionized water) on the leaching rate of Cu at S/L of 20%, leaching temperature of 30 °C, leaching time of 4 h, and stirring speed of 50 r/min. With the increase of H<sub>2</sub>SO<sub>4</sub> concentration, the leaching rate of Cu increased steadily and reached a maximum of 92.86% when the H<sub>2</sub>SO<sub>4</sub> concentration was 20%. However, when the H<sub>2</sub>SO<sub>4</sub> concentration was 10%, the pH of the leaching solution was –0.22, indicating that there was an excess of H<sup>+</sup> in the solution at that time. Moreover, the leaching rate of Cu at the H<sub>2</sub>SO<sub>4</sub> concentration of 10% was 88.99%, which was not significantly different from the H<sub>2</sub>SO<sub>4</sub> concentration was 20%. Therefore, to reduce the amount of Na<sub>2</sub>CO<sub>3</sub> solution used in the subsequent adjustment of pH, the optimal H<sub>2</sub>SO<sub>4</sub> leaching concentration was 10%.

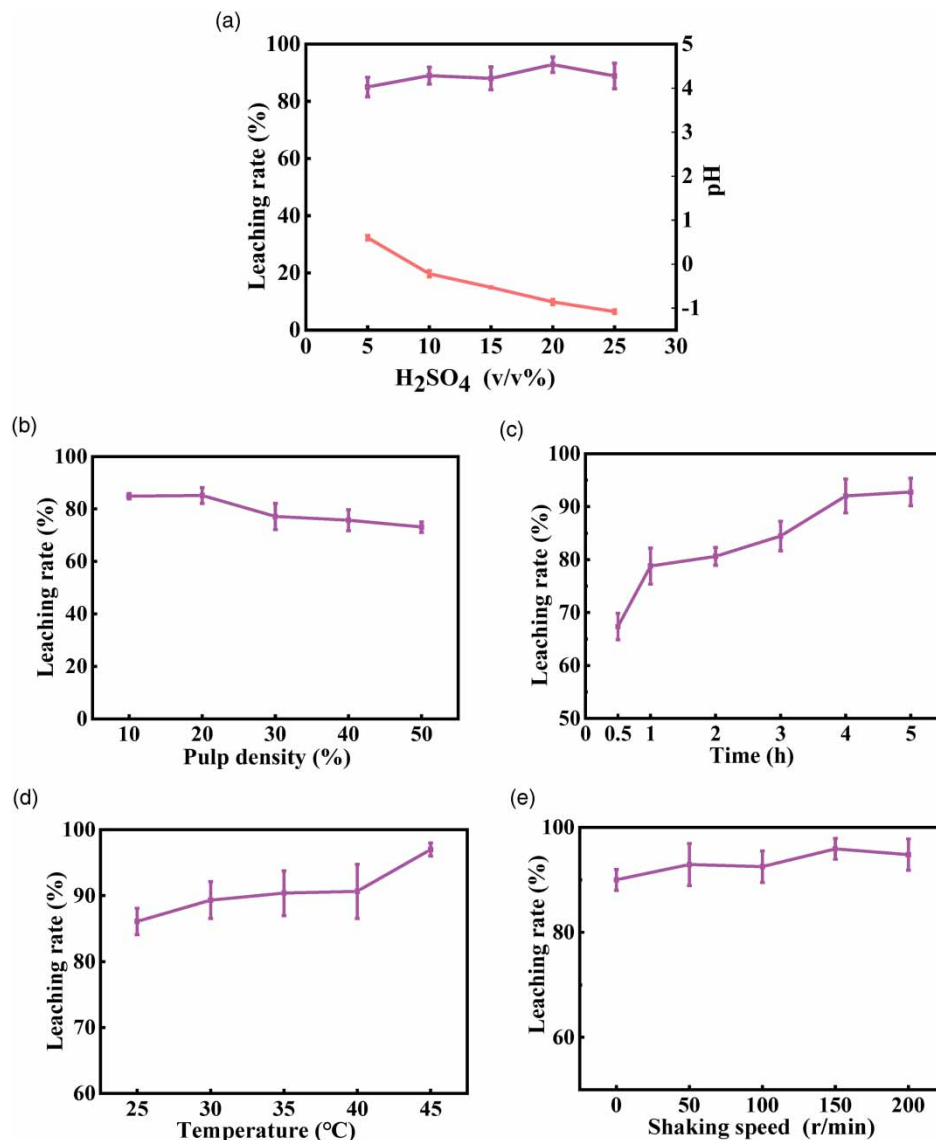
Figure 2(b) shows the effect of different S/L (10–50%) on the leaching rate of Cu at H<sub>2</sub>SO<sub>4</sub> concentration of 10%, leaching temperature time of 30 °C, leaching time of 4 h, and stirring speed of 50 r/min. With the increase of S/L, the leaching of Cu was first stabilized and then decreased. The leaching rate of Cu reached a maximum of 85.15% when S/L was 20%. As S/L increased, the difficulty of contact between H<sup>+</sup> and Cu in WCPR increased, and the reaction between H<sup>+</sup> and impurity ions

**Table 1** | Composition of WCPR after pretreatment (mass fraction, %)

Cu	Zn	Fe	Ca	Mg	Al	Na	K	Other
9.55	1.64	11.35	4.51	1.77	1.77	0.95	0.16	68.30



**Figure 1** | XRD diagram of WCPR.



**Figure 2** | Effect of sulfuric acid leaching process on the leaching rate of Cu: (a) sulfuric acid concentration, (b) pulp density, (c) leaching time, (d) leaching temperature, and (e) shaking speed.

increased, leading to a decrease in the leaching rate of Cu. In addition, the increase of S/L led to an increase in solids in the solution, which was not conducive to the subsequent separation, so the optimal leaching S/L was 20%.

Figure 2(c) shows the effect of different times (1–5 h) on the leaching rate of Cu at  $H_2SO_4$  concentration of 10%, S/L of 20%, leaching temperature of 30 °C, leaching time of 4 h, and stirring speed of 50 r/min. The leaching rate of Cu increased with the increase of leaching time, which increased rapidly in 0–1 h and increased slowly in 1–4 h. The leaching rate of Cu reached a maximum of 92.76% when the leaching time reached 4 h. When the leaching time reached 4 h, the leaching rate of Cu was stable and unchanged, so the optimal leaching time was 4 h.

Figure 2(d) shows the effect of different temperatures (25–45 °C) on the leaching rate of Cu at an  $H_2SO_4$  concentration of 10%, S/L of 20%, leaching time of 4 h, and stirring speed of 50 r/min. With the increase in temperature, the leaching rate of Cu remained basically unchanged. When the leaching temperature was 45 °C, the copper leaching rate of Cu increased to 95.66%, so the optimal leaching temperature was 45 °C.

Figure 2(e) shows the effect of different stirring speeds (0–200 r/min) on the leaching rate of Cu at an  $H_2SO_4$  concentration of 10%, S/L of 20%, leaching time of 4 h, and leaching temperature of 45 °C. With the increase of the stirring speed, the

leaching of Cu basically remained unchanged, so to release the generated gas as soon as possible, it was necessary to shake, and so the optimal stirring speed was 50 r/min.

Therefore, under the conditions of the  $\text{H}_2\text{SO}_4$  concentration of 10%, S/L of 20%, 150 min, leaching time of 4 h, leaching temperature of 45 °C, and stirring speed of 50 r/min, the best leaching rate of Cu (94.31%) could be ensured. However, as shown in Table 2, in addition to Cu (leaching concentration was 18.02 g/L), the leach solution also contained a large amount of Fe, Zn, Al, and Mg impurities.

### 3.3. Extraction of Cu from the leaching solution

As mentioned earlier, in addition to Cu, metals such as Fe, Ca, Zn, and Al were also present in the leach solution. Due to the abundance of metal elements in the leaching solution, it was not suitable to use impurity removal methods to achieve the recovery of Cu. However, the Cu extractant had the ability to form complexes with Cu ions at high pH (Liu *et al.* 2009) and could be recombined with  $\text{H}^+$  to release Cu ions at low pH (Liu *et al.* 2019). Therefore, the significant factors of pH, O/L, extraction time, and LIX984 concentration were selected to focus on their effects on the extraction rate of Cu, and the results are shown in Figure 3(a)–3(d), respectively.

Figure 3(a) shows the effect of different pH values (1–4) on the extraction rate of Cu at LIX984 concentration of 20% (LIX984: DT100, v/v), O/L of 2:1, and extraction time of 10 min. When the pH of the solution was in the range of 1–2, the extraction rate of Cu increased rapidly; after the pH of the solution was higher than 2.0, the extraction rate of Cu remained basically unchanged. When the solution pH was 1.0, the extraction rate of Cu was 84.76%; when the pH of the solution was 2.0, the extraction rate of Cu was 99.00%. Therefore, the optimal extraction pH was 2.0.

Figure 3(b) shows the effect of different O/L (1:1–5:1) on the extraction rate of Cu at a pH of 2.0, LIX984 concentration of 20%, and extraction time of 10 min. Similar to the effect of pH on Cu extraction, the extraction rate of Cu was 93.72% when O/L was 1:1 and reached 98.64% when O/L was 2:1. The extraction rate of Cu was basically around 99% as O/L continued to increase. By increasing the amount of extractant, the extraction rate of Cu was less than 1%. Therefore, the optimal O/L of 2:1 was more economical.

Figure 3(c) shows the effect of different extraction times (5–15 min) on the extraction rate of Cu at pH of 2.0, LIX984 concentration of 20%, and O/L of 2:1. With the increase of extraction time, the extraction of Cu first increased and then stabilized, and the extraction rate of Cu was 78.38% at 5 min and then reached the maximum of 99.51% at 10 min. Therefore, the optimal extraction time was 10 min.

Figure 3(d) shows the effect of different LIX984 concentrations (10–30%) on the extraction rate of Cu at pH of 2.0, O/L of 2:1, and extraction time of 10 min. With the increase of LIX984 concentration, the extraction rate of Cu fluctuated between 99 and 100%, meaning that a LIX984 concentration of 10% could already extract 99% of the Cu in the leach solution, so the optimal LIX984 concentration was 10%.

Therefore, as Table 3 shows, under the conditions of solution pH of 2.0, O/L of 2:1, extraction time of 10 min, and LIX984 concentration of 10%, the extraction rate of Cu reached 99.46%, and the Cu in the leaching solution was completely in the organic phase.

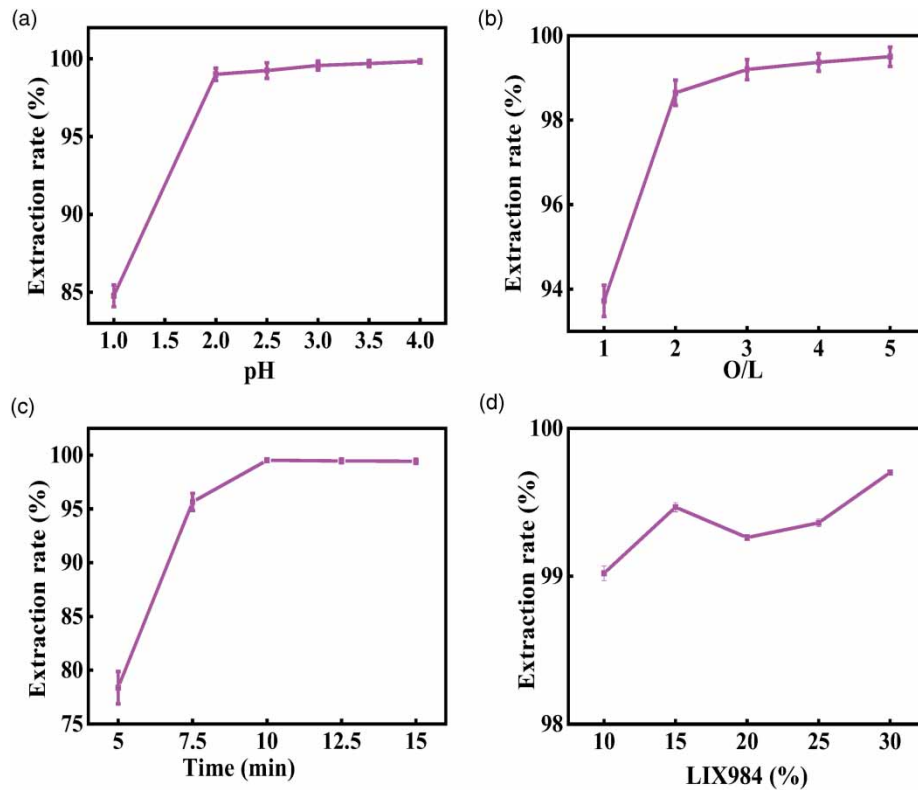
### 3.4. Stripping of Cu and preparation of $\text{CuSO}_4$

High concentrations of  $\text{H}_2\text{SO}_4$  could be used as a stripping agent to re-extract Cu ions from the organic phase back into the aqueous phase. Therefore, the significant factors of  $\text{H}_2\text{SO}_4$  concentration, stripping time, and O/L were selected to focus on their effects on the stripping rate of Cu, and the results are shown in Figure 4(a)–4(c), respectively.

Figure 4(a) shows the effect of different  $\text{H}_2\text{SO}_4$  concentrations (50–300 g/L) at the stripping rate of Cu at O/L of 1:1 and stripping time of 10 min. With the increase of  $\text{H}_2\text{SO}_4$  concentration, the stripping rate of Cu increased and then remained basically unchanged when the  $\text{H}_2\text{SO}_4$  concentration reached 200 g/L and above. When the concentration was 200 g/L, the stripping rate of Cu was 95.65%. The optimal  $\text{H}_2\text{SO}_4$  concentration was 200 g/L.

**Table 2** | Metal concentration in leaching solution under optimal conditions (g/L)

Cu	Zn	Fe	Ca	Mg	Al	Na	K
18.02	2.75	13.52	0.76	1.17	2.91	0.10	0.00



**Figure 3** | Effect of extraction process on the extraction rate of Cu: (a) pH, (b) O/L, (c) extraction time, and (d) LIX984 concentration.

**Table 3** | Metal concentration before and after extraction under optimal conditions (g/L)

	Cu	Zn	Fe	Ca	Mg	Al	Na	K
Before	11.26	2.24	11.20	0.49	1.04	2.00	33.25	0.00
After	0.06	1.72	8.45	0.48	0.73	1.82	24.89	0.00

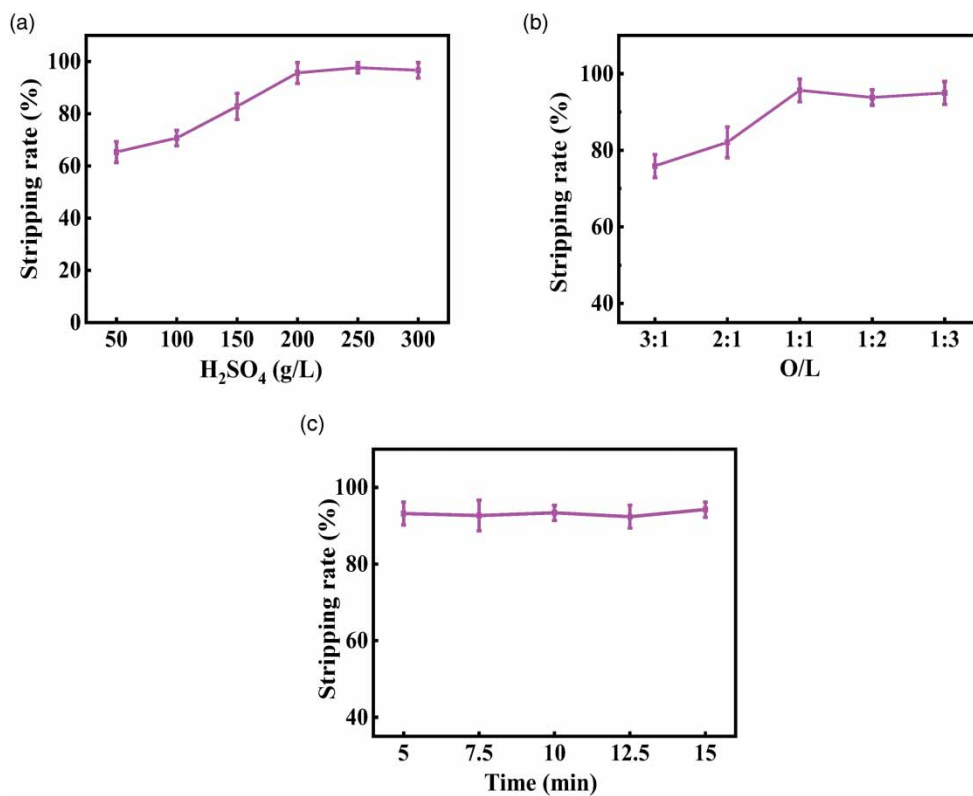
Figure 4(b) shows the effect of different O/L (3:1–1:3) on the stripping rate of Cu at  $\text{H}_2\text{SO}_4$  concentration of 200 g/L and stripping time of 10 min. As O/L decreased, the stripping rate of Cu first increased and then remained stable. When O/L was 3:1, the stripping rate of Cu was 75.90%, and when O/L was 1:1, the stripping rate of Cu increased to 95.65%. When O/L was lowered again, the stripping rate of Cu did not increase, so using an O/L of less than 1:1 to strip Cu would waste a part of the  $\text{H}_2\text{SO}_4$  solution. Therefore, the optimal O/L was 1:1.

Figure 4(c) shows the effect of different stripping times (5–15 min) on the stripping rate of Cu at  $\text{H}_2\text{SO}_4$  concentration of 200 g/L and O/L of 1:1. With the increase of the stripping time, the stripping rate of Cu was basically a straight line, and the stripping rate of Cu was basically around 92%. Therefore, the optimal stripping time was 5 min.

As shown in Table 4, under the optimal stripping conditions of  $\text{H}_2\text{SO}_4$  concentration of 200 g/L, O/L of 1:1, and stripping time of 5 min, the concentration of Cu was 6.14 g/L, and the stripping rate of Cu was 95.32%. Since the solution was essentially free of other metal impurity ions, the solution was then heated, evaporated, cooled, and crystallized to obtain aqueous  $\text{CuSO}_4$  crystals. Figure 5 shows the XRD diagram of aqueous  $\text{CuSO}_4$ , in which the peaks were very narrow, indicating that the resulting  $\text{CuSO}_4$  was well crystallized.  $\text{CuSO}_4$  had a wide range of applications as a raw material for the production of other Cu salts, as a catalyst for the production of pigments and fragrances, in the flotation of non-ferrous metals, in the preparation of electronic-grade Cu foils, as a fungicide, and so on.

### 3.5. Characterization and utilization of leaching residue of WCPR

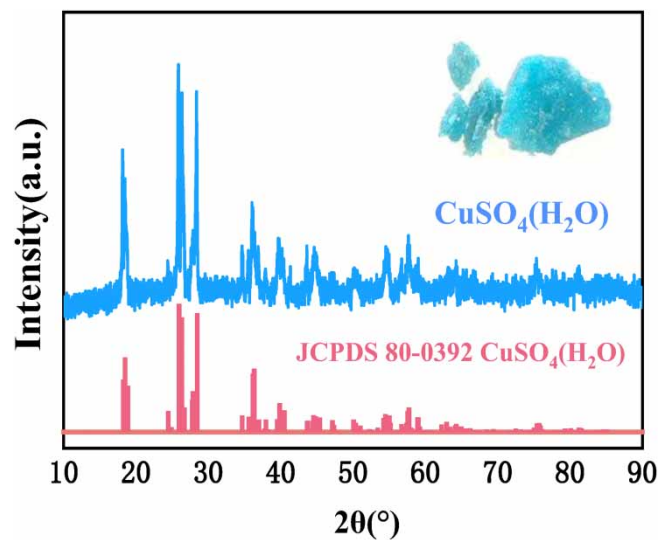
The leaching toxicity test results for the leaching residue of WCPR are presented in Table 5. The concentration of Cu was 50.23 mg/L, and the concentration of Zn was 21.38 mg/L, both of which were lower than the standard limit of 100 mg/L,



**Figure 4** | Effect of the stripping process on the stripping rate of Cu: (a) sulfuric acid concentration, (b) O/L, and (c) stripping time.

**Table 4** | Metal concentration under optimal stripping conditions (g/L)

Cu	Zn	Fe	Ca	Mg	Al	Na	K
6.14	0.00	0.00	0.01	0.00	0.06	0.19	0.00



**Figure 5** | XRD diagram of  $CuSO_4(H_2O)$ .

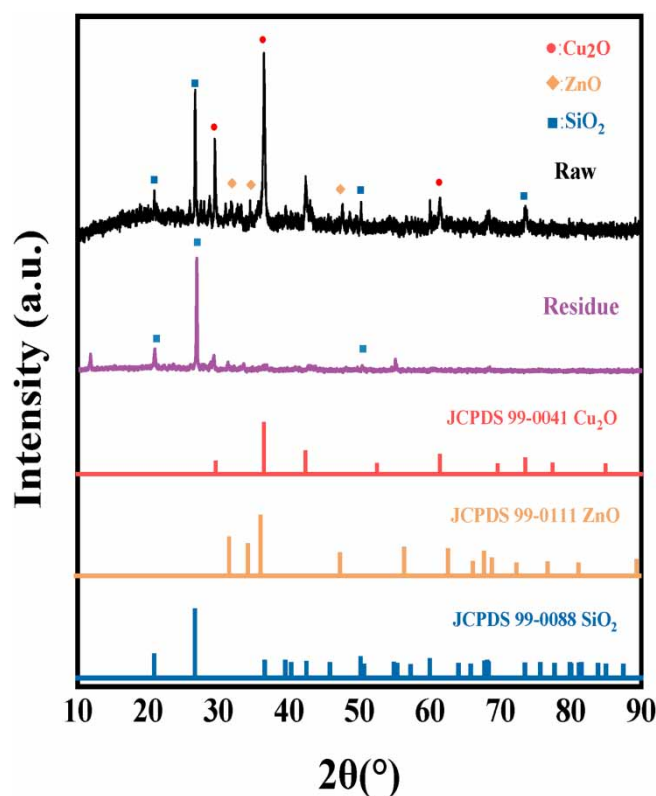


indicating that the leaching residue of WCPR contained trace amounts of Cu and Zn, but there was no more leaching toxicity. The XRD characterization of WCPR before and after leaching is shown in Figure 6; the peaks of  $\text{Cu}_2\text{O}$  and  $\text{ZnO}$  could be seen before leaching, and only the peak of  $\text{SiO}_2$  could be seen after leaching, indicating that there was still  $\text{SiO}_2$  in the leached residue. The same conclusion could be obtained by observing the SEM images of WCPR before and after leaching. As shown in Figure 7(a), the morphology of WCPR was irregular and the composition was relatively complex. The composition of each block was relatively concentrated, with some blocks having a high Ca content and some blocks containing more Fe. The distribution of Zn and Cu was relatively dispersed and uniform, with no particularly concentrated areas. Figure 7(b) shows that the size of the blocks in the leaching residue was obviously reduced, and the presence of Zn and Cu was almost invisible. The content of Fe has also decreased significantly, while the content of O, Si, and Ca in the leaching residue was still high. This was also consistent with the XRD results.

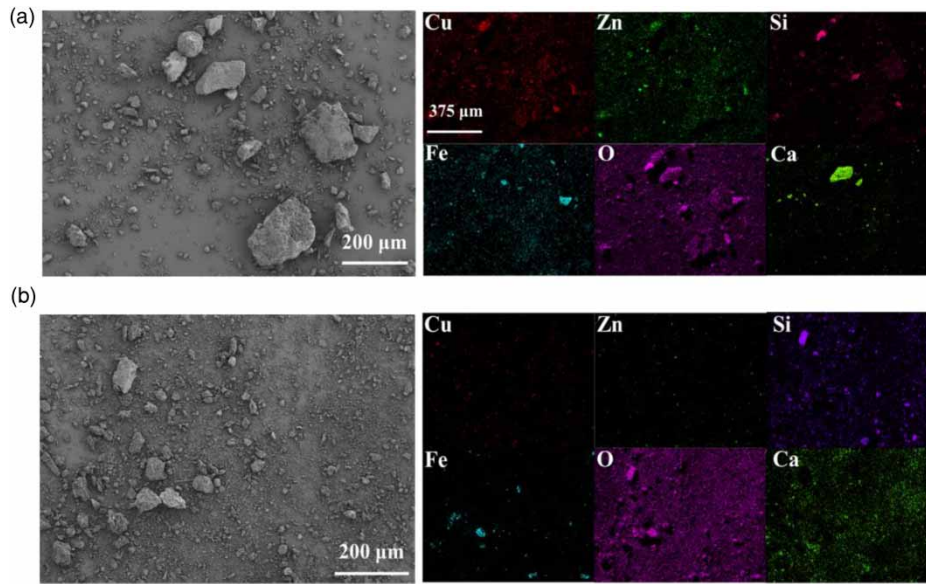
The FT-IR characterization of WCPR before and after leaching is shown in Figure 8, and the diagram had underwent significant changes before and after leaching. Before the leaching of WCPR, there was only a relatively obvious stretching vibration peak of the Si-O-Si group corresponding to  $1,024\text{ cm}^{-1}$ . After leaching, stretching vibration peaks of -OH appeared at  $3,540$  and  $3,403\text{ cm}^{-1}$ , corresponding to  $-\text{CH}_2$  stretching vibration peak at  $2,927\text{ cm}^{-1}$ , C=O group stretching vibration peak at  $1,721\text{ cm}^{-1}$ , C=C group absorption peak at  $1,623\text{ cm}^{-1}$ , and C-O group absorption peak at  $1,130\text{ cm}^{-1}$  (Wu & Li 2004; Li *et al.* 2021). Currently, Wuxi self-polishing antifouling paint is the commonly used antifouling paint, which was most commonly used for hydrolysable resin acrylic or methacrylic acids (Xu *et al.* 2011). The functional groups contained in acrylic acid correspond to the peaks of the functional groups determined by infrared analysis, so the leaching residue of WCPR was mainly acrylic acid or methacrylic acid resin,  $\text{SiO}_2$ , as well as a small amount of Ca, Fe, and other substances. The leaching residue of WCPR could be used for cement kiln incineration, thus realizing the high-value utilization of WCPR.

**Table 5** | Test results of leaching toxicity of leaching residue of WCPR (mg/L)

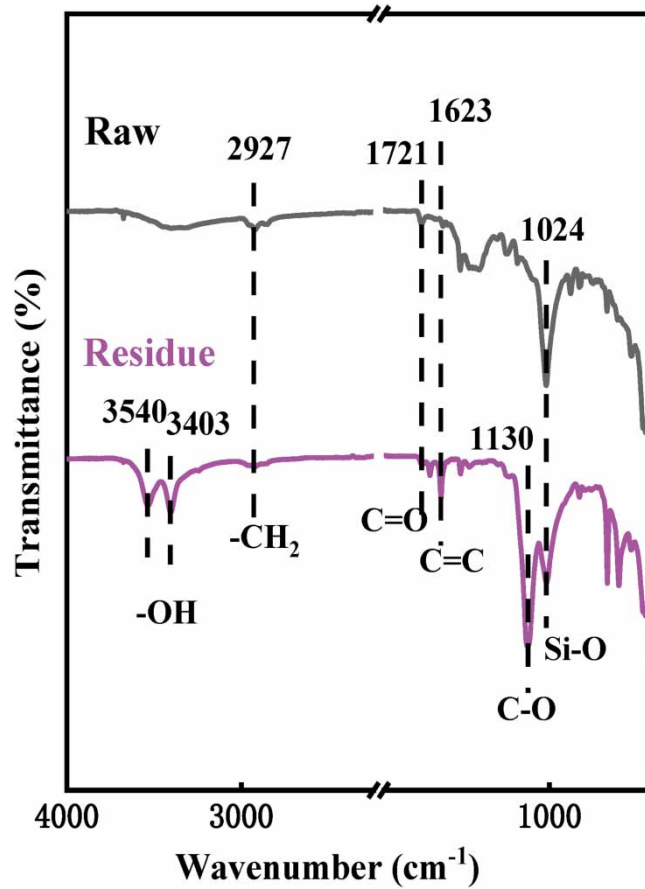
Cu	Zn	Fe	Ca	Mg	Al	Na	K
50.23	21.38	12.34	330.28	38.23	0.00	5.02	0.00



**Figure 6** | XRD diagram of WCPR before and after leaching.



**Figure 7** | SEM images of WCPR before and after leaching: (a) before and (b) after.



**Figure 8** | FT-IR diagram of WCPR before and after leaching.

#### 4. CONCLUSION

Cu was an indispensable basic material in modern industry, but the increasing depletion of copper mines had led to an increase in the production costs of Cu materials. As a result, the recovery of Cu from solid wastes even hazardous wastes containing Cu for the production of valuable Cu materials has attracted great concern around the world. Considering the enormous amount of WCPR and the high concentration of Cu contained in it, the efficient utilization of WCPR as a secondary resource to produce Cu materials was preferred, which had the benefits of eliminating Cu pollution and recovering the Cu resource. In this article, WCPR was taken as the research object, and  $\text{CuSO}_4$  was prepared by the sulfuric acid leaching extraction stripping process, so as to provide a theoretical basis for the recovery of Cu in WCPR. The conclusions were as follows:

- (1) WCPR contained a large amount of Cu, and it mainly existed in the form of  $\text{Cu}_2\text{O}$ . However, due to its high dispersion and complex distribution, it was often chelated with organic compounds and was difficult to directly utilize. Under the optimal leaching conditions at  $\text{H}_2\text{SO}_4$  concentration of 10%, S/L of 20%, leaching time of 4 h, leaching temperature of 45 °C, and stirring speed of 50 r/min, the leaching concentration of Cu was 18.02 g/L and the leaching rate was 94.31%.
- (2) Due to the large variety and quantity of metal ions in the leaching solution, it was not suitable to use the step-by-step precipitation method to remove impurity ions, so the solvent extraction method was selected to recover Cu from the leaching solution. Under the optimal extraction conditions at pH of 2.0, O/L of 2:1, extraction time of 10 min, and LIX984 concentration of 10%, the extraction rate of Cu reached 99.46% and Cu in the leaching solution completely entered the organic phase. The leaching solution of separated Cu could be mixed with the leaching solution of WCPR and then continued to remove iron and precipitate Zn. Under the optimal stripping conditions at an  $\text{H}_2\text{SO}_4$  concentration of 200 g/L, O/L of 1:1, and stripping time of 5 min, the concentration of Cu was 6.14 g/L and the stripping rate was 95.32%. The  $\text{CuSO}_4$  crystal was obtained by evaporating, cooling, and crystallizing the stripping solution.
- (3) The toxicity leaching concentration of Cu in the leaching residue was 50.23 mg/L, and the concentration of Zn was 21.38 mg/L, which was below the standard limit of 100 mg/L, indicating that the leaching residue of WCPR had no leaching toxicity. It mainly consisted of acrylic or methacrylic resin,  $\text{SiO}_2$ , and a small amount of Ca, Fe, and other substances. The leaching residue of WCPR could be used for cement kiln incineration, thereby achieving a high-value utilization of WCPR.

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#### CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Gongchu Shi: conceptualization, methodology, investigation, writing – original draft. Lingkai Wen: writing – review & editing. Shihao Zhang: resources. Jian Cheng: validation, visualization, and formal analysis. Xiaohui Chen: validation. Yanyu Zhou: formal analysis. Zhikai Xu: writing – review & editing. Baoping Xin: writing – review & editing and supervision.

#### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

#### CONFLICT OF INTEREST

The authors declare there is no conflict.

#### REFERENCES

- Arce, R., Galan, B., Coz, A., Andres, A. & Viguri, J. R. 2010 *Stabilization/solidification of an alkyd paint waste by carbonation of waste-lime based formulations*. *J. Hazard. Mater.* **177** (1–3), 428–436. <https://doi.org/10.1016/j.jhazmat.2009.12.050>.
- Avcı, H., Ghorbanpoor, H., Topcu, I. B. & Nurbas, M. 2017 *Investigation and recycling of paint sludge with cement and lime for producing lightweight construction mortar*. *J. Environ. Chem. Eng.* **5** (1), 861–869. <https://doi.org/10.1016/j.jece.2017.01.009>.
- Blanca, A. 2008 *Environmental levels, toxicity and human exposure to tributyltin (TBT)-contaminated marine environment. A review*. *Environ. Int.* **34** (2), 292–308. <https://doi.org/10.1016/j.envint.2007.09.005>.
- Chen, L., Chen, S., Niu, Y., Lin, J., Yang, M. & Liu, Y. 2021 *Research progress of marine antifouling biocides*. *Dev. Appl. Mater.* **36** (5), 94–102. <https://doi.org/10.19515/j.cnki.1003-1545.2021.05.012>.

- Davey, P. T. & Scott, T. R. 1976 Removal of iron from leach liquors by the 'Goethite' process. *Hydrometallurgy* **2** (1), 25–33. [https://doi.org/10.1016/0304-386X\(76\)90011-6](https://doi.org/10.1016/0304-386X(76)90011-6).
- Dvořák, P. & Jandová, J. 2005 Hydrometallurgical recovery of zinc from hot dip galvanizing ash. *Hydrometallurgy* **77** (1–2), 29–33. <https://doi.org/10.1016/j.hydromet.2004.10.007>.
- Fu, Z. 2012 Discussion on the treatment and disposal methods of paint waste residue. *Henan Chem. Ind.* **29** (Z5), 28–29. <https://doi.org/10.14173/j.cnki.hnhg.2012.z5.023>.
- Gerace, M. & Gerace, J. 1992 Method of making a filler from automotive paint sludge, filler, and sealant containing a filler. U.S. Patent: U.S., 5160628.
- Li, H., Zhang, C., Tian, W. & Lei, J. 2021 Research on preparation of anti-ultraviolet coatings based on polymethyl methacrylate and its properties. *J. Xi'an Univ. (Nat. Sci. Ed.)* **24** (4), 50–54. <https://doi.org/10.3969/j.issn.1008-5564.2021.04.010>.
- Liu, Y., Zhang, G., Liu, Z., Li, J., Cao, H. & Li, W. 1992 Method of making a filler from automotive paint sludge, filler, and sealant containing a filler. U.S. Patent: U.S., 5160628.
- Liu, Q., Yu, R., Fang, Z. & Chen, A. 2009 Extractants in copper hydrometallurgy technology. *Nonferr. Met. Eng.* **61** (2), 88–92. <https://doi.org/10.3969/j.issn.2095-1744.2009.02.023>.
- Liu, Y., Zhang, G., Liu, Z., Li, J., Cao, H. & Li, W. 2019 Study on extraction of Cu in waste etching solution by LIX984. *Nonferr. Met. Eng.* **9** (11), 32–38. <https://doi.org/10.3969/j.issn.2095-1744.2019.11.006>.
- Maia, F., Silva, A. P., Fernandes, S., Cunha, A., Almeida, A., Tedim, J., Zheludkevich, M. L. & Ferreira, M. G. S. 2015 Incorporation of biocides in nano-capsules for protective coatings used in maritime applications. *Chem. Eng. J.* **270**, 150–157. <https://doi.org/10.1016/j.cej.2015.01.076>.
- Mohamed, S. S., Sherif, A. E., Maher, A. E., Ahmed, I. H., Ossama, M. A. E., Ashraf, M. E. & Nesreen, A. F. 2015 Modeling of spherical silver nanoparticles in silicone-based nanocomposites for marine antifouling. *RSC Adv.* **5** (78), 63175–63185. <https://doi.org/10.1039/c5ra07400b>.
- Niu, T., Wang, J., Chu, H., Qian, C., Duan, N., Gadd, G. M., Shi, W. & Xin, B. 2021 Deep removal of arsenic from regenerated products of spent V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> SCR catalysts and its concurrent activation by bioleaching through a novel mechanism. *Chem. Eng. J.* **420**, 127722. <https://doi.org/10.1016/j.cej.2020.127722>.
- Qian, X., Dong, R., Tang, F. & Dong, Y. 2015 Review on treatment of the automotive paint wastes. *Ind. Safety Environ. Prot.* **41** (2), 52–55 + 102. <https://doi.org/10.3969/j.issn.1001-425X.2015.02.017>.
- Rosli, N., Abd, R. & Kadri, A. 2018 Methane synthesis from automotive paint sludge via microwave-assisted pyrolysis. *Mater. Sci. Eng.* **358** (1), 012029. <https://doi.org/10.1088/1757-899X/358/1/012029>.
- Saft, R. J. 2007 Life cycle assessment of a pyrolysis/gasification plant for hazardous paint waste. *Int. J. Life Cycle Assess.* **12**, 230–238. <https://doi.org/10.1065/lca2007.05.332>.
- Salihoglu, G. & Salihoglu, N. K. 2016 A review on paint sludge from automotive industries: Generation, characteristics and management. *J. Environ. Manage.* **169**, 223–235. <https://doi.org/10.1016/j.jenvman.2015.12.039>.
- Song Y., Woo J., Park S. & Kim, I. S. 2005 A study on the treatment of antifouling paint waste from shipyard. *Mar. Pollut. Bull.* **51** (8–12), 1048–1053. <https://doi.org/10.1016/j.marpolbul.2005.02.017>.
- Su, X., Qin, F., Cai, F., Ma, C. & Tang, C. 2020 Preparation of nano-sized zinc oxide by thermal decomposition with different carbonate precipitates. *Inorg. Chem. Ind.* **51** (9), 36–39. <https://doi.org/10.11962/1006-4990.2018-0600>.
- Tian, B., Cui, Y., Qin, Z., Wen, L., Li, Z., Chu, H. & Xin, B. 2022 Indirect bioleaching recovery of valuable metals from electroplating sludge and optimization of various parameters using response surface methodology (RSM). *J. Environ. Manage.* **312**, 114927. <https://doi.org/10.1016/j.jenvman.2022.114927>.
- Wang, Y. & Dai, J. 2020 Research on the common methods and advantages and disadvantages of minimizing treatment of paint residues in ship painting. *Chin. High New Tech.* **20**, 115–117. <https://doi.org/10.13535/j.cnki.10-1507/n.2022.20.41>.
- Wang, Y., Zhu, H. & Jiang, Y. 2018 Research situation and development of co-processing of hazardous waste in cement kiln. *Environ. Pollut. Ctrl.* **40** (8), 943–949. <https://doi.org/10.15985/j.cnki.1001-3865.2018.08.019>.
- Wu, C. & Li, H. 2004 Synthesis research and characterization of low-molecular weights poly-acrylic acid sodium. *J. Anhui Univ. Sci. Tech. (Nat. Sci.)* **1**, 71–74. <https://doi.org/10.3969/j.issn.1672-1098.2004.01.017>.
- Xing, P., Ma, B., Wang, C., Wang, L. & Chen, Y. 2018 A simple and effective process for recycling zinc-rich paint residue. *Waste Manage.* **76**, 234–241. <https://doi.org/10.1016/j.wasman.2018.03.018>.
- Xu, J., Yu, L., Li, X. & Yang, Y. 2011 Development of self-polishing antifouling coatings and evaluation approaches. *Paint Coat. Ind.* **41** (12), 62–66. <https://doi.org/10.3969/j.issn.0253-4312.2011.12.015>.
- Yi, L., Zhao, L., Xu, Y. & Li, X. 2019 Leaching and solvent extraction of copper from electroplating sludge. *Mining Metal. Eng.* **39** (4), 115–118, 122. <https://doi.org/10.3969/j.issn.0253-6099.2019.04.027>.
- Yuan, Y. & Wang, X. 2015 Recycling of paint residue. *Recyclable Res. Cir. Econ.* **8** (1), 34–37. <https://doi.org/10.3969/j.issn.1674-0912.2015.01.011>.
- Zhao, Y., Zhan, J., Liu, G., Ren, Z., Zheng, M., Jin, R., Yang, L., Wang, M., Jiang, X. & Zhang, X. 2017 Field study and theoretical evidence for the profiles and underlying mechanisms of PCDD/F formation in cement kilns co-incinerating municipal solid waste and sewage sludge. *Waste Manage.* **61**, 337–344. <https://doi.org/10.1016/j.wasman.2016.12.008>.